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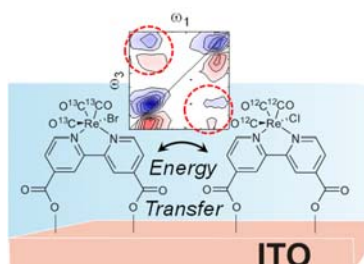
# Ultrafast Vibrational Energy Transfer in Catalytic Monolayers at Solid-Liquid Interfaces

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## Abstract

We investigate the ultrafast vibrational dynamics of monolayers from adsorbed Rhenium-carbonyl CO<sub>2</sub>-reduction catalysts on a semiconductor surface (Indium-Tin-Oxide (ITO)) with ultrafast 2D ATR IR spectroscopy. The complexes are partially equipped with isotope-labelled (<sup>13</sup>C) carbonyl ligands to generate two spectroscopically distinguishable forms of the molecules. Ultrafast vibrational energy transfer between the molecules is observed via the temporal evolution of cross-peaks between their symmetric carbonyl stretching vibrations. These contributions appear with time constant of 70 ps and 90 ps for downhill and uphill energy transfer, respectively. The energy transfer is thus markedly slower than any of the other intramolecular dynamics. From the transfer rate, an intermolecular distance of ~4-5 Å can be estimated, close to the van der Waals distance of the molecular head groups. The present paper presents an important cornerstone for a better understanding of intermolecular coupling mechanisms of molecules on surfaces and explains the absence of similar features in earlier studies.



TOC Graphic

## Keywords:

Rhenium carbonyl complexes, heterogeneous CO<sub>2</sub> reduction catalysts, vibrational energy transfer, surface vibrational spectroscopy, 2D ATR IR spectroscopy, intermolecular cross peaks.

Heterogeneous catalysis is a main area of research in current chemistry.<sup>1-7</sup> In particular molecular structure and dynamics of catalysts as well as reactants at solid-liquid interfaces are of importance for catalytic processes, for instance in the field of renewable energy production. A major chemical process in catalysis is the photo-electrochemical conversion of CO<sub>2</sub>.<sup>8-16</sup> In heterogeneous systems, catalyst molecules often are covalently immobilized at surfaces. It is however typically not known precisely if, and through which mechanisms, adsorbate molecules can interact with each other, or with their environment. In this paper, we demonstrate vibrational excitation energy transfer between CO<sub>2</sub> reduction catalysts, which are immobilized at a semiconductor surface. By use of 2D ATR IR spectroscopy<sup>17-19</sup>, we clearly identify vibrational energy transfer via cross-peaks between catalyst molecules with different vibrational frequencies. This type of incoherent energy transfer takes place on the timescale of nearly hundred picoseconds and is thus markedly slower than any other intramolecular dynamics.

We have recently introduced 2D ATR IR as a new method for surface vibrational spectroscopy with sub-picosecond temporal resolution.<sup>17-19</sup> Similar to 2D IR in bulk solution<sup>20-23</sup>, 2D ATR IR is a variant of four-wave-mixing spectroscopy and is thus based on the third-order nonlinear susceptibility of the sample. In variance to transmission-type methods, 2D ATR IR is based on evanescent waves, which are generated at the interface between a high and a low refractive index material upon internal reflection.<sup>24-26</sup> Being a third-order nonlinear spectroscopy, 2D ATR IR is sensitive to all molecules within a certain distance from the interface, i.e. the penetration-depth of the evanescent wave, which can range up to several micrometers off the surface.<sup>24-26</sup> Under these circumstances, immobilization of the sample at the interface allows obtaining surface-sensitive signals from solid-liquid interfaces. With this approach, we have recently investigated the ultrafast vibrational dynamics of surface-bound carbon monoxide<sup>17,27</sup> and cyanide<sup>28</sup> as well as self-assembled organic monolayers under various conditions<sup>18,19,29,30</sup>.

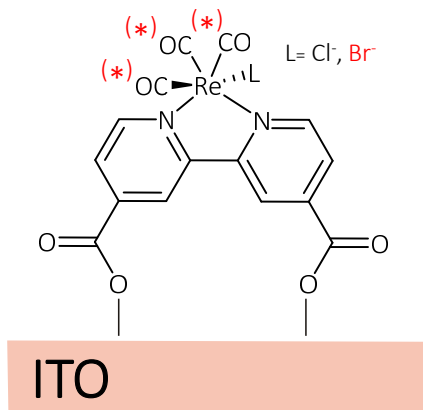


Figure 1. Sample molecule  $\text{Re}(4,4'\text{-dicarboxyl-2,2'-bipyridine})(\text{CO})_3\text{L}$  immobilized on an Indium-Tin-Oxide (ITO) surface.  $\text{L} \equiv \text{chloride} (\text{Cl}^-)$  or bromide ( $\text{Br}^-$ ). In case of the naturally abundant  $^{12}\text{CO}$  ligands, the axial ligand is  $\text{Cl}^-$ , for the  $^{13}\text{C}$  labeled compound it is  $\text{Br}^-$  (in red).

The sample under investigation in the present study is  $\text{Re}(4,4'\text{-dicarboxyl-2,2'-bipyridine})(\text{CO})_3\text{L}$  ( $\text{Re}(\text{CO})_3\text{L}$ , with  $\text{L} = \text{Cl}^-$  or  $\text{Br}^-$ ), see Fig. 1. This type of Re-carbonyl complexes are of importance as photo- and electro-catalysts for  $\text{CO}_2$ -reduction<sup>31,32</sup> or as sensitizers in solar cells<sup>33,34</sup>. We prepared two molecules, one with the naturally abundant  $^{12}\text{CO}$  ligands (and with  $\text{L}=\text{Cl}^-$ ) and one fully labelled  $^{13}\text{CO}$  ligands, where the isotope exchange required  $\text{L}=\text{Br}^-$ .<sup>35</sup> The molecules were bound to the oxide vacancies of an indium-tin-oxide (ITO) layer via their two carboxylate functional groups. To that end, a 5 nm thin ITO layer was sputter-coated on the reflecting plane of a  $\text{CaF}_2$  ATR prism, resulting in a nanoparticle structure with diameters between 2 nm and 10 nm (see scanning electron microscopy image in Figure 2 (a)). In contrast to sputtered metal layers, which have been extensively used in previous reports of 2D ATR IR<sup>29,36</sup>, plasmonic signal enhancement effects are negligible for a pure ITO layer. The two molecules are co-adsorbed on a surface with roughly equal concentrations, as determined from the in-situ measured ATR IR absorbance (Figure 2 (b)).

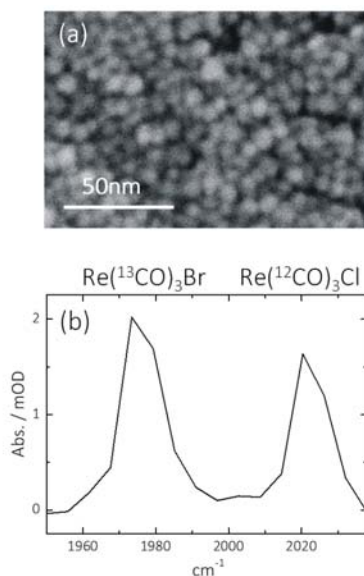


Figure 2. (a) SEM image of a sputter-coated indium-tin-oxide (ITO) layer on a CaF<sub>2</sub> substrate with an average thickness of 5 nm. (b) In-situ measured ATR IR absorption of co-adsorbed Re(<sup>13</sup>CO)<sub>3</sub>Br and Re(<sup>12</sup>CO)<sub>3</sub>Cl on ITO and immersed in methanol (MeOH).

Figure 3 shows 2D ATR IR spectra of (a) Re(<sup>13</sup>CO)<sub>3</sub>Br, (b) Re(<sup>12</sup>CO)<sub>3</sub>Cl, and (c) a ca. 1:1 mixture of both molecules (the latter being same as in Fig. 2 (b)). We focus on the symmetric stretching vibration of the carbonyl ligands, which red-shifts by 46 cm<sup>-1</sup> upon isotope labelling from about 2022 cm<sup>-1</sup> to 1976 cm<sup>-1</sup> (the axial ligand, Cl<sup>-</sup> vs. Br<sup>-</sup>, has essentially no effect on the vibrational frequency). The 2D ATR IR signals exhibit the usual ground state bleach/stimulated emission contribution (GSB/SE, blue) along with an excited state absorption band (ESA, red). These two features appear strongly elongated along the diagonal line, which is indicative for strong inhomogeneous broadening of the sample.<sup>20</sup> The heterogeneity is caused by the different local environments and structures of the molecules attached to various sized and morphologies of the ITO nanoparticles (Figure 2 (a)).

Each complex adsorbed alone on the surface results in a single symmetric stretch band with no substructure (the same can be deduced also from the absorption spectrum shown in Fig. 2 (b)). Furthermore, the spectrum of the mixture equals a trivial sum of those of the individual species (Figure 3), and finally, no cross-peaks between the symmetric stretch vibrations of the two molecules are detectable in the 2D ATR IR spectra at an initial population time of 0.25 ps (Figure 3 (c)). These observations indicate that first, the coupling between molecules is weak, and that second, each molecule exists as a single species on the surface, in contrast to previous related studies, which differ in the way how the samples have been prepared.<sup>37–39</sup>

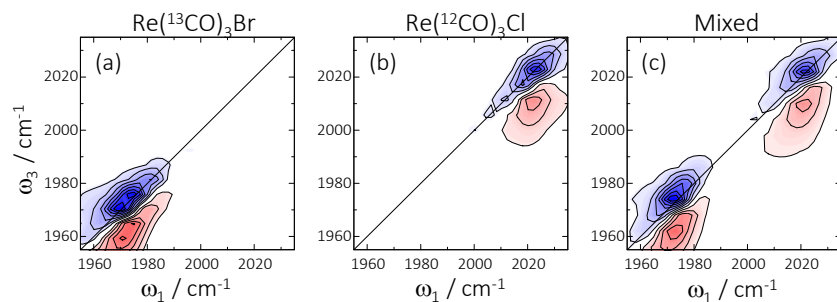


Figure 3. Normalized 2D ATR IR spectra of (a)  $\text{Re}^{(13}\text{CO})_3\text{Br}$ , (b)  $\text{Re}^{(12}\text{CO})_3\text{Cl}$  and (c) a 1:1 mixture of both co-adsorbed on an ITO-coated  $\text{CaF}_2$  prisms immersed in MeOH at a population delay of 0.25 ps.

But even when coupling is too weak to result in direct cross-peaks at early population times, vibrational energy transfer may occur as a result of fluctuations in the coupling Hamiltonian (in analogy to NOESY in NMR), that reveals cross-peaks growing in as a function of population time.<sup>20,40–42</sup> To explore that effect, Figure 4 shows a time-series of 2D ATR IR spectra, where indeed distinct cross-peaks show up above and below the diagonal after a few picoseconds ((b) - (d)). With increasing population delays, these cross peaks decay similar as the diagonal peak features (see below).

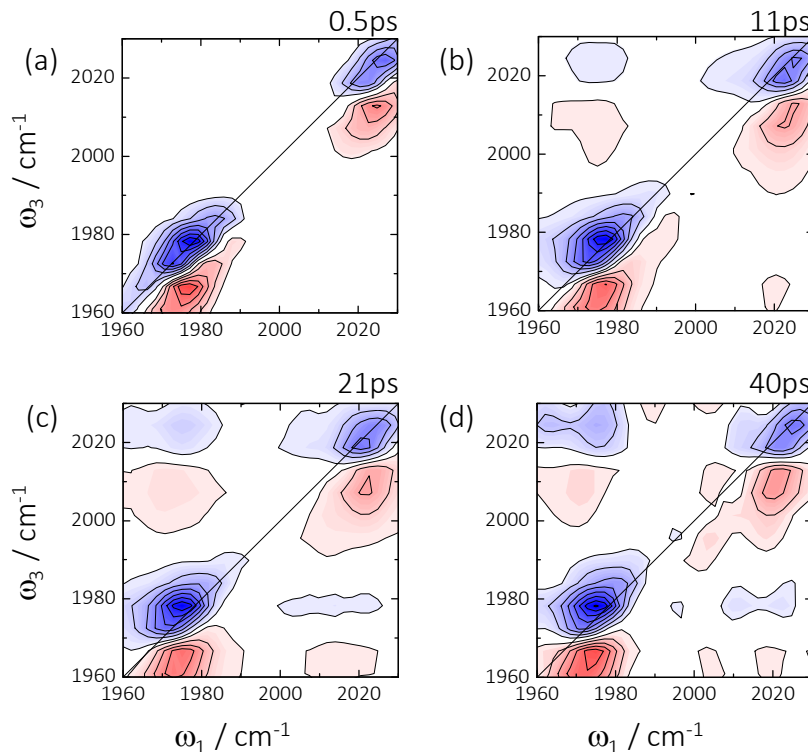


Figure 4. 2D ATR IR spectra for the co-adsorbed complexes  $\text{Re}^{(12}\text{CO})_3\text{Cl}$  and  $\text{Re}^{(13}\text{CO})_3\text{Br}$  on 5 nm ITO surfaces on a  $\text{CaF}_2$  prism immersed in MeOH at indicated population delays. Blue/red signals correspond to GSB/SE and ESA contributions, respectively. Cross-peaks between the two different molecules appear with increasing population delays. Signals have been normalized to maximum ground-state bleach intensity at each population delay.

Before being able to unambiguously assign these cross-peaks to intermolecular vibrational energy transfer, it is necessary to rule out other possibilities for their origin. In particular, it has been shown that if molecules are immobilized on a surface, relaxation-induced heat generated in the substrate can give rise to cross-peaks between different adsorbate bands.<sup>28,41</sup> Such signals originate from a response (e.g. a frequency-shift and broadening) of the vibrational lineshape of all adsorbate modes on the surface to the substrate temperature. However, these thermal effects persist for much longer timescales than vibrational relaxation, since diffusive cooling of the substrate is slow. This makes it possible to discriminate between heat signals and vibrational excitation via the underlying dynamics.<sup>28</sup> Figure 5 shows IR-pump-IR-probe signals of the symmetric CO stretch vibration of  $\text{Re}^{(12}\text{CO})_3\text{Cl}$  and  $\text{Re}^{(13}\text{CO})_3\text{Br}$  up to population delays much longer ( $> 200$  ps) than vibrational relaxation (20 ps). The absence of any long-lived signals in the data clearly rules out temperature effects, presumably since the CO ligands are too far away from the substrate (in contrast to the CO molecules directly bound to a Pt-surface in ref. <sup>28</sup>).



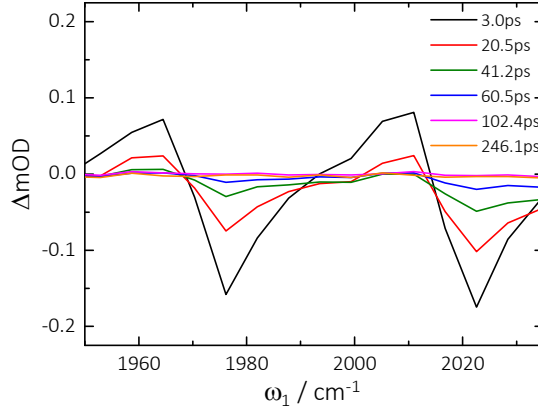


Figure 5. Selected IR-pump/IR-probe transient absorption spectra in the symmetric CO stretch region of co-adsorbed  $\text{Re}(^{13}\text{CO})_3\text{Br}$  and  $\text{Re}(^{12}\text{CO})_3\text{Cl}$  on ITO at indicated population delays. The signals decay completely to zero without any long-lived thermal signal contribution.

With that, we now turn to a kinetic analysis of the diagonal and cross-peak 2D ATR IR features shown in Figure 4. Figure 6 (a) and (b) shows kinetic traces obtained from the full time series of 2D ATR IR spectra with population delays up to 60 ps. Open circles represent the dynamics of the diagonal peak of (a)  $\text{Re}(^{13}\text{CO})_3\text{Br}$  and (b)  $\text{Re}(^{12}\text{CO})_3\text{Cl}$ , whereas open triangles correspond to the cross-peaks between them. Note that the cross peak intensities have been magnified by a factor of 5. The diagonal signals decay monotonically, whereas the cross-peak signals start from zero, increase initially, go through a maximum at about 17 ps and decay afterwards. The data are fitted with a model of coupled relaxation pathways as shown in Figure 6 (c). Once excited, both molecules undergo relaxation to the vibrational ground state (with the same time constants  $\tau_{1,2}$  for  $\text{Re}(^{13}\text{CO})_3\text{Br}$  and  $\text{Re}(^{12}\text{CO})_3\text{Cl}$ , respectively) or via energy transfer to the corresponding other molecule (with time constants  $\tau_{\text{ET},\text{fw}}$   $\tau_{\text{ET},\text{bw}}$  for forward and backward energy transfer, respectively). From the data, vibrational relaxation of both molecules is determined to proceed bi-exponentially with a fast contribution ( $\tau_{\text{fast}1,2} = 3$  ps) and a slow contribution ( $\tau_{\text{slow}1,2} = 20$  ps) and with an amplitude ratio of about 0.3/0.7, respectively. A bi-exponential relaxation with similar relative amplitudes has been observed before for analogous Rhenium tri-carbonyl-complexes both in bulk solution environment as well as for surface-bound molecules,<sup>43–45</sup> and has been attributed to intra-molecular vibrational energy redistribution (IVR) between the symmetric and asymmetric stretching modes of the carbonyl ligands.<sup>44</sup> Our model assumes that vibrational energy transfer can take place during both fast as well as slow relaxation pathways. A global fit of the data reveals time constants for vibrational energy transfer of  $\tau_{\text{ET},\text{fw}} = 90$  ps and  $\tau_{\text{ET},\text{bw}} = 70$  ps, where the ratio of these two numbers is in excellent agreement with detailed-balance:

$$\frac{k_{\text{ET},\text{bw}}}{k_{\text{ET},\text{fw}}} = \exp\left(-\frac{\Delta\omega}{k_B T}\right) \approx 0.8 \quad (1)$$

given a frequency separation of  $\Delta\omega = 46 \text{ cm}^{-1}$ . Intermolecular energy transfer is therefore significantly slower than any other process. Taking into account the vastly different timescales for the energy transfer and the fast component of vibrational relaxation (3 ps) together with its comparatively low relative amplitude, the initial phase of intra-molecular vibrational equilibration contributes only negligibly to the total energy transfer process.

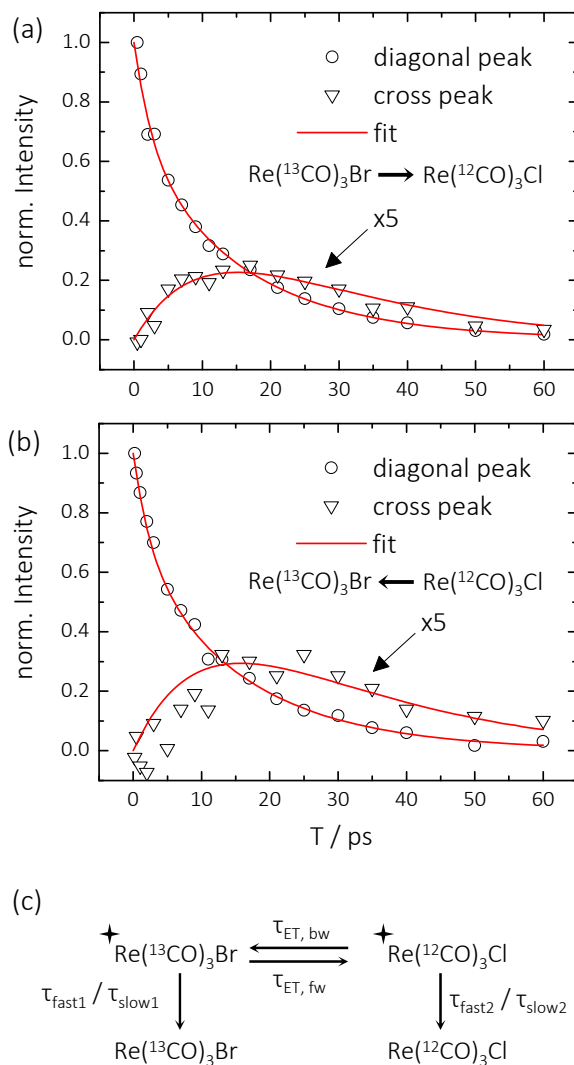


Figure 6. (a) Kinetic traces obtained from the diagonal peak (open circles) and cross-peak (open triangles) of a full series of 2D ATR IR spectra of  $\text{Re}(^{12}\text{CO})_3\text{Cl}$  and  $\text{Re}(^{13}\text{CO})_3\text{Br}$  on 5 nm ITO surfaces on a  $\text{CaF}_2$  prism immersed in MeOH. Red lines correspond to exponential fits with a model schematically depicted in (b). The star denotes vibrational excitation.

Based on these cross-relaxation time constants, we can give a rough estimate of the intermolecular donor-acceptor distances. The time constant for the energy transfer is theoretically described<sup>46</sup> by:

$$\frac{1}{\tau_{DA}} = k_{DA} = \frac{2}{1 + \exp\left(\frac{-\Delta\omega}{k_B T}\right)} V^2 \frac{\tau^{-1}}{\Delta\omega^2 + 4V^2 + \tau^{-2}} \quad (2)$$

where  $\Delta\omega$  is the frequency difference between the donor and acceptor (46 cm<sup>-1</sup>),  $\tau^{-1}$  is the dephasing linewidth of the donor/acceptor transitions that can be estimated from the anti-diagonal width of the 2D ATR IR spectra (10 cm<sup>-1</sup>), and  $V$  is approximated as transition dipole coupling between the donor and the acceptor modes:

$$V^2 = \frac{1}{n^4} \frac{\kappa^2 \mu_D^2 \mu_A^2}{(4\pi\epsilon_0)^2 r_{DA}^6} \quad (3)$$

Here,  $\kappa^2$  is an orientational factor, which we assume to be 1 for a staggered configuration on the surface,  $n$  is the refractive index,  $\epsilon_0$  is the vacuum permittivity,  $\mu_{D/A}$  are the transition dipole moments of the donor/acceptor transitions, respectively, and  $r_{DA}$  is the donor/acceptor distance. The transition dipoles can be estimated from the absorption band (extinction coefficient 3400 M<sup>-1</sup> cm<sup>-1</sup>, width 14 cm<sup>-1</sup>),<sup>20</sup> revealing 0.47 D. With these values, we obtain a donor/acceptor distance of  $r_{DA} \approx 4-5$  Å, which suggests that the molecules are in fairly close proximity on the surface; i.e. essentially at the van der Waals distance of the molecular head groups. As a caveat, it should be noted that with that set of parameters, one estimates  $V=10$  cm<sup>-1</sup>, which is so large that one would expect a direct cross-peak at early delay times, whose intensity relative to a diagonal peak scales as  $4V^2/\Delta\omega^2$ .<sup>20</sup> Since we however do not observe any direct cross peak, we assume that Eq. 3 overestimates the coupling, which is counter-balanced by the fact that cross-relaxation can proceed to more than one coupling partner on the surface (the model Fig. 6 c assumes only two interacting molecules). Nonetheless, despite the huge uncertainties in this model, the very steep  $1/r_{DA}^6$  dependence of the rate still renders the (probably systematic) error in the estimate of  $r_{DA}$  relatively small.

Despite significant efforts reported in literature<sup>30,47-49</sup>, intermolecular couplings of surface-bound molecules have only rarely been observed<sup>38</sup>, and the estimates given above help to understand why that is so. In the present case, we can observe cross peaks with good signal-to-noise ratio, but this is since we have the very strong transition dipole of the symmetric stretch vibration of a metal-carbonyl together with (presumably) a close to optimal packing on the surface. The transition dipole enters as 4<sup>th</sup>-power in Eq. 3, and the inter-molecular distance as the 6<sup>th</sup>-power, hence, if either one of it is reduced/increased by just a small amount, the vibrational energy transfer rate will be too slow to be observed in the short time window set by vibrational relaxation.

We are aware of only one other study on a very similar Re(CO)<sub>3</sub>Cl system on a TiO<sub>2</sub> surfaces, for which intermolecular cross-peaks have been observed.<sup>38</sup> In that case, two absorption peaks have been obtained already for a single chemical species without any isotope labelling, for reasons that are not totally clear (different binding sites as well as couplings between aggregates have been discussed as possible reason for the two peaks).<sup>38,39,50</sup> Weak cross peaks have been identified between these two peaks already at the earliest population delay (0 ps) together with tentative coherent oscillations in their

intensities as a function of population time, indicating an inter-molecular coupling that is strong enough to mix the vibrational states.<sup>38</sup> This is in clear variance to the data presented here in several aspects. First, we observe only a single peak for the symmetric stretch vibration of either one of the two molecules on ITO surfaces immersed in methanol (*Figure 3*). This allows us to definitely assign the origin of each one of the two peaks to a monomeric species. Second, we do not detect any initial cross-peaks (e.g., at 0.25 ps and 0.5 ps), rather, we observe only incoherent vibrational energy transfer for significantly longer population delays (the range of population times in ref.<sup>38</sup> was too short to conclude whether the same would happen in that case as well). It should also be noted that ref.<sup>38</sup> is in fact the third in a series on basically the same molecular system, with no detectable couplings in the preceding papers,<sup>39,50</sup> suggesting that intermolecular couplings strongly depend on the preparation procedure that affects both surface morphology and surface coverage.

A counterexample regarding intermolecular interactions are monolayers equipped with  $\text{Re}(\text{CO})_3\text{Cl}$  head-groups separated from the surface by short linear alkyl-spacers (i.e., alkyl-chains with three and 11 carbon atoms).<sup>47,48,51,52</sup> According to our results, a possible explanation for these observations is that such spacers introduce a significant degree of structural flexibility, which influences intermolecular distances and orientations through packing effects of the alkyl chains. In particular, intermolecular distances of around 7.5 Å have been estimated for the monolayers with alkyl-chains.<sup>48</sup> Assuming a similar set of parameters regarding intermolecular coupling as discussed above would slow down energy transfer to  $\tau_{\text{ET}} \approx 800$  ps. The large structural flexibility might render the intermolecular distances just a bit larger, yet unobservable due to the very strong distance dependence in Eq. 3. Finally, monolayer systems on a noble metal surfaces equipped with azide IR labels were investigated in the same context, as here employing isotope labelling to reveal spectroscopically distinguishable molecules.<sup>19</sup> The transition dipole is a factor 2.5 lower in this case, and at the same time the vibrational lifetime is much shorter with only 1.5 ps, explaining why vibrational energy transfer could not be observed either.

In summary, we have investigated the ultrafast vibrational dynamics of monolayers from a Rhenium-carbonyl-based  $\text{CO}_2$ -reduction catalysts on Indium-Tin-Oxide (ITO) surfaces by use of 2D ATR IR spectroscopy. Isotope-labelling of the carbonyl ligands was used to generate two different forms of the catalyst molecule at the interface, which exhibit distinctive vibrational bands for the symmetric CO stretching vibration. Vibrational energy transfer was observed between the different catalyst molecules by the appearance of population-time dependent cross-peaks in the 2D ATR IR spectra. The forward and backward energy transfer dynamics within a molecular monolayer on a surface is quantified with a time constant of 70 ps / 90 ps, respectively, which is significantly slower than any of the intramolecular dynamics. In analogy to NOESY in NMR, the transfer rate can be used to roughly estimate an intermolecular distance of 4-5 Å. Our results can be used to explain the absence of intermolecular cross-peaks in other 2D IR experiments of molecular monolayers.

The observation of intermolecular interactions between adsorbates, such as the ones described here, is of significant importance for a broad range of applications in heterogeneous catalysis<sup>2,3,5,7</sup>, molecular recognition<sup>53–55</sup>, chemical sensing<sup>56–58</sup> or sensitization<sup>33,59,60</sup>. Particularly for potentially catalytically-active systems, the ultrafast intramolecular vibrational dynamics of Re-carbonyl complexes in electronic ground and excited states have been investigated in detail before, mainly for bulk solution samples, but recently also for immobilized systems under a variety of experimental conditions.<sup>37–39,45,47,48,50,52,61–65</sup> However, intermolecular dynamics are largely unexplored to date, since femtosecond multi-dimensional vibrational spectroscopy on surfaces became available only recently.<sup>17,47,48,66</sup> Nonetheless, it has been proposed that if the vibrational states of two molecules are coupled, the electronic states will be as well, which in turn may have a decisive impact on the performance of working devices.<sup>38,39</sup> In the context of catalysis, e.g. CO<sub>2</sub> reduction, it is clear that more than one electron has to be accumulated at a single site, again requiring coupling between the molecules that will depend on spatial proximity. In future experiments, it will be interesting to see to what extent vibrational coupling correlates with catalytic activity.

## Experimental

The details of our 2D ATR IR setup have been described in detail before.<sup>17–19</sup> Briefly, the output of a mid-IR OPA is split into pump- and probe beams, which are spatially overlapped at the reflecting plane of a single-reflection CaF<sub>2</sub> ATR substrate, and the probe beam is detected behind the sample with a 32-pixel MCT array detector. A Mach-Zehnder interferometer is used to generate pump-pulse pairs for two-dimensional spectroscopy.<sup>67</sup> Scanning the delay between the two pump pulses is used to generate fully absorptive pump-probe 2D ATR IR spectra.

To immobilize the sample at the ITO surfaces, the sputter-coated ATR substrates were incubated overnight in a 0.1 mM solution (10 mL) in methanol (MeOH). The ATR substrates were then sonicated for 10 minutes in MeOH, thoroughly washed and kept in pure solvent before and during the measurements. Isotope-substitution of the carbonyl ligands in Re(<sup>13</sup>CO)<sub>3</sub>Br was achieved by stirring a solution of [NEt<sub>4</sub>]<sub>2</sub>[ReBr<sub>3</sub>(<sup>12</sup>CO)<sub>3</sub>] in dimethylformamide for three weeks under a <sup>13</sup>CO atmosphere, forming [NEt<sub>3</sub>][ReBr<sub>2</sub>(<sup>13</sup>CO)<sub>4</sub>] as described in a previous work.<sup>35</sup> Re(<sup>12</sup>CO)<sub>5</sub>Cl and [NEt<sub>3</sub>][ReBr<sub>2</sub>(<sup>13</sup>CO)<sub>4</sub>] were then used to synthesize Re(<sup>12</sup>CO)<sub>3</sub>Cl / Re(<sup>13</sup>CO)<sub>3</sub>Br according to published procedures.<sup>68</sup>

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